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An Evaluation of the Organochoromium Content of Sewage Sludge

Monsanto Research Corp, Dayton, OH

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16. ABSTRACT

The organochromium content of sewage sludge was evaluated during this study. Sewage sludges containing chromium were obtained. These sludges were analyzed to determine total chromium and then fractionated to obtain four chromium fractions. The fractions represented soluble chromium, cationic chromium which was dilute acid soluble, and alkali soluble and insoluble fractions. The two later fractions represent the chromium which is associated with humus and humin respectively.

Mixtures of the sludges were analyzed for total and fractionated chromium. These mixtures were then subjected to aerobic and anaerobic digestion for 30 days. After the 30 day period the sludge mixtures were reanalyzed.

Good mass balances were obtained for both the distribution of chromium among fractions compared with total chromium analyses and between before and after digestion samples. Data also was collected from the four fractions described earlier (for twenty-two other elements). These data were collected for sludge mixtures both before and after digestion studies. Comparisons were made of the distribution of the various elements.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS			b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
chromium	cadmium	phosphorus		
sewage	cobalt	antimony		
sludge	copper	silicon		
analysis	iron	strontium		
silver	magnesium	titanium		
aluminum	manganese	yttrium		
boron	molybdenum	zinc		
barium	nickel	atomic absorption		
beryllium	lead	ICAP		

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The organochromium content of sewage sludge was evaluated during this study. Sewage sludges containing chromium were obtained. These sludges were analyzed to determine total chromium and then fractionated to obtain four chromium fractions. The fractions represented soluble chromium, cationic chromium which was dilute acid soluble, and alkali soluble and insoluble fractions. The two later fractions represent the chromium which is associated with humus and humin respectively.

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SECTION 1

SUMMARY

The objective of this study was to evaluate the organochromium content of sewage sludge. There are three important questions to be answered in order to better understand the fate of chromium in sewage treatment plants: First, is there formation and subsequent loss of volatile organochromium compounds resulting in transferral of chromium from the treatment plant to the surrounding environment during aeration or digestion processes? Second, is the chromium being effectively removed from the aqueous portion of the sewage during treatment? Third, what is the molecular form of the chromium which is associated with the sludge from the treatment processes? The answers to questions one and two were determined during the study. The volatile organochromium compounds, if present, would have been collected on a porous polymer resin during simulated aerobic and anaerobic digestion studies. Distribution of chromium between aqueous and solid fractions at various points throughout the sewage treatment plant was determined as a partial answer to question two. In response to question three, experiments were devised to determine the distribution of chromium in sludges among soluble, cationic (acid soluble), alkali soluble and nonalkali soluble fractions. This fractionation was performed before and after simulated aerobic and anaerobic digestions.

While the mass balances obtained for the study were good, an original objective of obtaining high performance liquid chromatography-atomic absorption (HPLC-AA) information concerning polarity and molecular weight distribution for the organochromium

compounds was not met because it was not possible to raise the chromium content of the aqueous layer by concentration techniques.

In the four fractions listed earlier, information was also obtained with regard to the distribution of 22 other elements. All results were obtained for both before and after samples from both aerobic and anaerobic digested sludges.

SECTION 2

INTRODUCTION

The evaluation of the organochromium content of sewage sludge was conducted by Monsanto Research Corporation (MRC) in response to Research Request No. 3 of Contract No. 68-01-1980 with the United States Environmental Protection Agency's Office of Toxic Substances (EPA/OTS). During Research Request No. 1 of the same contract MRC had sampled the sewage sludge at the City of Dayton Guthrie Road sewage treament plant (1). The study had determined the total chromium and the chromium in the diethyl ether extractable portion of the sludge. The diethyl ether extractable portion was found to contain only 1% of the total chromium in the sludge. In order to more fully understand the fate of chromium during sewage treatment the study described in this report was undertaken.

There are three important questions to be answered in order to better understand the fate of chromium in sewage treatment plants: First, is there formation and subsequent loss of volatile organochromium compounds resulting in transferral of chromium from the treatment plant to the surrounding environment during aeration or digestion processes? Second, is the chromium being effectively removed from the aqueous portion of the sewage during treatment? Third, what is the molecular form of the chromium which is associated with the sludge from the treatment processes? The answers to questions one and two were determined during the study. The volatile organochromium compounds, if present, would have been collected on a porous polymer resin during simulated aerobic and anaerobic digestion studies. Distribution of chromium between aqueous and solid fractions at

various points throughout the sewage treatment plant was determined as a partial answer to question two. In response to question three, experiments were devised to determine the distribution of chromium in sludges among soluble, cationic (acid soluble), alkali soluble and nonalkali soluble fractions. This fractionation was performed before and after simulated aerobic and anaerobic digestions. The results from each of these studes are detailed in the following background, experimental, and results and discussion sections.

SECTION 3

BACKGROUND

In typical municipal sewage treatment facilities, flocculation and coagulation processes tend to concentrate most of the heavy metal content of the incoming wastes into the solid particulate that is eventually removed as sewage sludge. Stones (2) found that 28% of the incoming chromium was removed by sedimentation. In a comparison study he found that removal of chromium was influenced by the chemical treatment of the sewage. His results are listed in Table 1. In a later study Stones (3) found that activated sludge treatment was superior to biofiltration for removal of chromium. He also found an average of 70% removal of chromium for four different types of activated sludge treatment.

TABLE 1. REMOVAL OF CHROMIUM BY VARIOUS CHEMICAL TREATMENT PROCESSES (2)

Process	Percent removal
Settlement	22
Calcium oxide (CaO)	49
Sulfuric acid (H_2SO_4)	29
Aluminum sulfate [$Al_2(SO_4)_3$]	63

Most generally studies of the trace metal content of sewage sludge have reported the total concentrations of the various metals based on ashing or digestion techniques, both of which isolate the metals from the sample matrix. Other more specific studies (4, 5) have investigated the water and acetic acid extractability of metals in sludge as an indication of their

availability for plant uptake. However, in most cases these techniques recover <10% of the total metal content.

It is known (6, 7) that a large part of the metal content of sludge exists as soluble and insoluble metal-organic complexes. These complexes have not been characterized in detail but are generally similar to trace metal-organic complexes existing in soil and involve bonding through principally carboxyl, phenolic and imide functional groups in the organic matter.

Studies have been made to determine the nature of the organic content of secondary sewage treatment effluents. Painter et al. (8) and Bunch et al. (9) found that about 35% of the organics were ether extractable proteins, carbohydrates, tannins, lignins, and detergents. Rebhun and Manka (10) found that 40-50% of the organic material could be classified as humic substances (humic, fulvic and hymathomelanic acids) of which fulvic acid was a major fraction. Gel permeation studies showed that the majority of the fulvic and hymathomelanic acids had molecular weights in the range 500-1000, with the majority of the humic acids being in the range of 10,000-50,000.

Newland et al. (11) have determined the concentration of selected trace metals associated with various organic fractions of sewage sludge. The concentrations of Cd, Cu, Mn, Ni, and Zn were determined in humic acid, β-humus (insoluble fulvic acid), soluble fulvic acid, and humin (alkali-insoluble residue) fractions of sewage sludge obtained by the fractionation procedure described by Black (12). Their results showed that the organic matter in sewage sludge had the following composition:

humin	70%
fulvic acid	20%
humic acid	8%

The trace metal analysis showed that the humic acid fraction contained the lowest amount of trace metals. They concluded that contrary to what had often been speculated, the humic acid fraction is not responsible for large amounts of organically bound metals. The humin fraction, in general, gave the highest metal content.

Chromium is commonly found in sewage sludges in concentrations ranging from 50 to 500 µg/g (13). The nature of this chromium content has not been well established. It is of considerable interest, however, since the form in which the chromium exists has particular importance to the ultimate fate of the chromium in the environment (e.g., availability for plant uptake, susceptibility to leaching, or even volatility).

3.1 PROPOSED APPROACH

MRC proposed to conduct four studies to evaluate the chromium content of a sewage sludge sample.

(A) Total Chromium Determination
(B) Organic Extractable Chromium
(C) Humic Material Fractionation
(D) Aerobic/Anaerobic Digestion

The sewage sludge samples were obtained from the City of Dayton Guthrie Road sewage treatment plant, located ∿1.6 km from the MRC Dayton Laboratory. This was one of the sites previously sampled in Task I of EPA Contract No. 68-01-1980 (see Reference 1 for details). Total chromium concentration for the sludge sample from this site analyzed in the previous study was 620 µg/g.

3.2 DESCRIPTION OF THE SEWAGE TREATMENT PLANT

The City of Dayton Guthrie Road sewage treatment plant, Guthrie Road, Dayton, Ohio 45418, was chosen for sampling because the City of Dayton Water Department personnel stated that the bulk of chromium waste they receive is handled by this facility. The plant occupies a site of approximately 640 m x 1280 m. There are two major buildings on the site, one housing offices and a laboratory and the second housing the control room and maintenance facilities. Various other small buildings, approximately 20 large trickle bed filters, and several large sludge pits are also located on the site.

The plant is bounded on the north by Guthrie Road, an open field and Madden Golf Course; on the east by West River Road, an open field and the Great Miami River; and on the south and west by open fields and wooded areas. The closest industry is on the opposite bank of the Great Miami River and consists of light industry, an asphalt batch plant, sand and gravel operations, and storage warehouses.

Guthrie Road sewage treatment plant handles waste from the City of Dayton and other sections of Montgomery County including Englewood and Trotwood. The major contributors of chromium in the wastewater processed by this facility are chrome platers and large industry such as General Motors and Chrysler installations in the area serviced.

The plant operates continously and discharges 190,000-230,000 m^3/day of treated wastewater through an open concrete ditch into the Great Miami River. The average water retention time in the plant is $\sim$4.5 hours. The outfall is very turbulent and significantly affects the flow of the river at the point of entry and for some distance downstream.

The City of Dayton Guthrie Road sewage treatment plant is located in southwestern metropolitan Dayton, Ohio area approximately 16 km south of the intersection of Interstates 70 and 75. The immediate area around the plant site has a relatively low population concentration which increases as one moves toward the Dayton population center. The City of Dayton is located in a river valley at the junction of the Miami, Mad, and Stillwater Rivers. The general topography is flat. The metropolitan area has a population of about 865,000 and supports an impressive diversity of industry. There are some 850 plants located in Montgomery County producing over 1000 different products with an estimated value of over $1 billion annually. Major industries in the area include automotive subassembly, appliance manufacturing, and precision equipment manufacturing.

SECTION 4

EXPERIMENTAL

The objective of the experimental portion of this study was to evaluate the organochromium content of sewage sludge. In order to more carefully characterize the sewage tratment plant, samples were taken at various points throughout the plant. The locations and descriptions of the sampling points are listed in Section 4.1. The simulated digester experiments performed during the study are described in Section 4.2. Fractionation and extraction procedures are described in Section 4.3. Analytical procedures including a description of the atomic absorption detector for liquid chromatography are described in Section 4.4.

4.1 SAMPLING TREATMENT PLANT

Six sites were sampled at the Guthrie Road sewage treatment plant. Figure 1 shows an aerial photograph of the plant with the location of the sampling sites. The six sample locations were the influent, influent to primary, influent to secondary, influent to secondary clarifier, effluent from secondary clarifier, and effluent. These samples were collected in polypropylene bottles and returned to the laboratory. Each sample was shaken and a representative aliquot (25 ml) removed. Each sample was then filtered through 0.2-μm filters and the aqueous fraction analyzed by atomic absorption.

The filtrates and solids were digested with a 1 to 1 mixture of concentrated nitric and sulfuric acids in Teflon beakers. Small quantities of hydrofluoric acid were added to aid in the

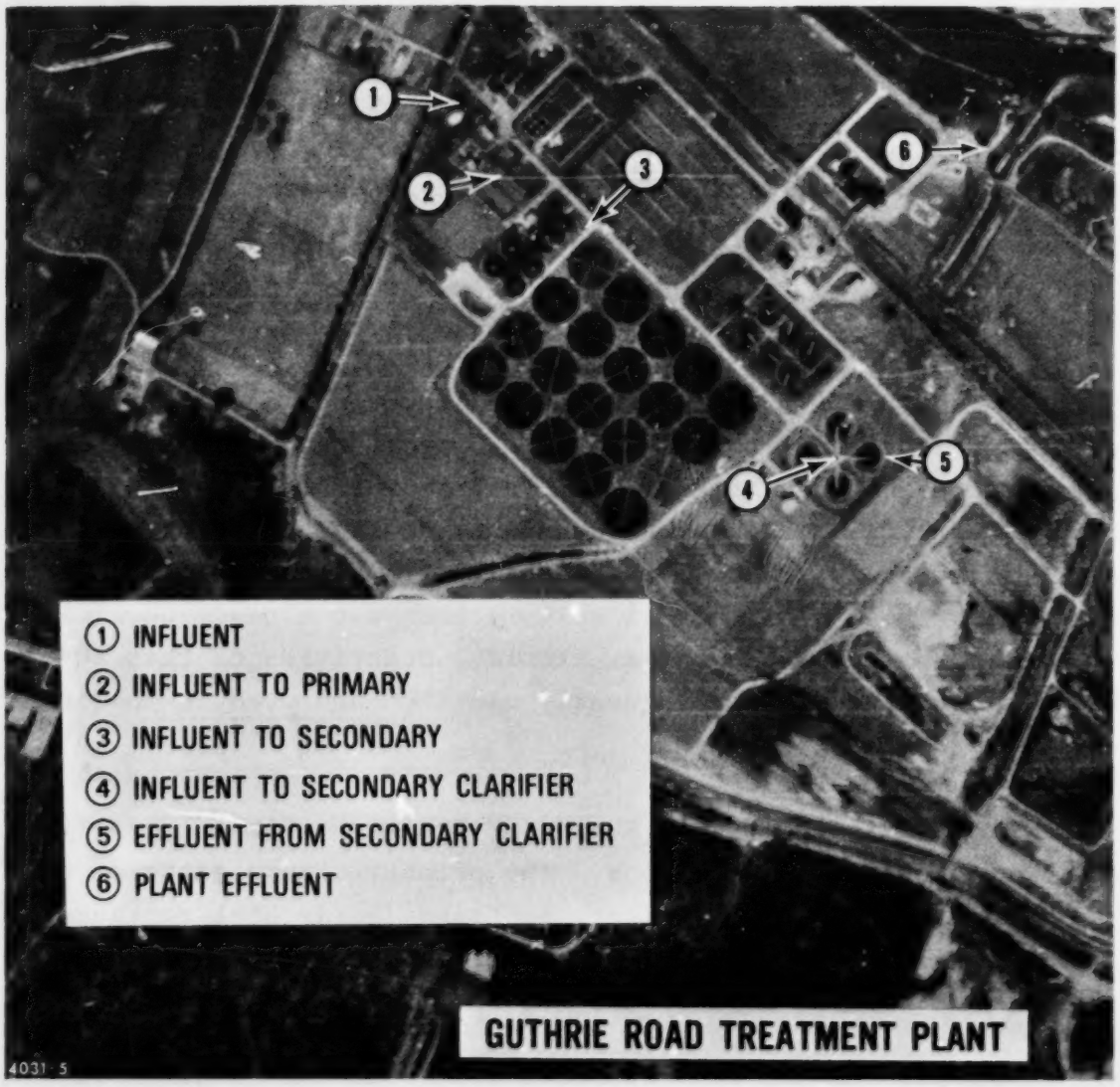


Figure 1. Aerial view of Guthrie Road sewage treatment plant with sampling locations.

digestion of silica. Results of this study are described in the Results and Discussion section.

4.2 AEROBIC AND ANAEROBIC DIGESTION

In order to insure that samples obtained from aerobic and anaerobic digestion runs were as representative as those obtained from actual municipal operations, the procedures used in the laboratory centered on utilizing biological cultures in use at actual area waste treatment plants,

4.2.1 Anaerobic Digestion

Through contact with Mr. Defro Tossey, Superintendent, Division of Sewage Treatment, Dayton, Ohio, information was gathered to indicate that the existing anaerobic digesters at the City of Dayton Municipal Treatment Plant are currently operating on sludges (entirely primary) that contain high concentrations of chromium. Thus, a biological culture that was already acclimated to high chromium levels was available. Quantities of this acclimated culture were subsequently obtained and used as the inoculum for the laboratory run.

Most chromium in the Dayton Municipal Treatment Plant comes from area metal treating operations. The primary sludge gathered at the sludge outlet of the primary settling (horizontal rectangular) tanks thus contains substantial chromium. Quantities of this sludge were used as feed to the laboratory digester.

The apparatus used in the anaerobic digestion run is shown in Figure 2. A 5000-ml reactor flask was placed in a water bath which was heated with an immersion heater. Water temperature in the bath was maintained through the use of a rheostat to insure a temperature of 35°C (± 2°C) in the reactor flask itself. The bath-reactor flask was positioned on a magnetic stirrer to insure

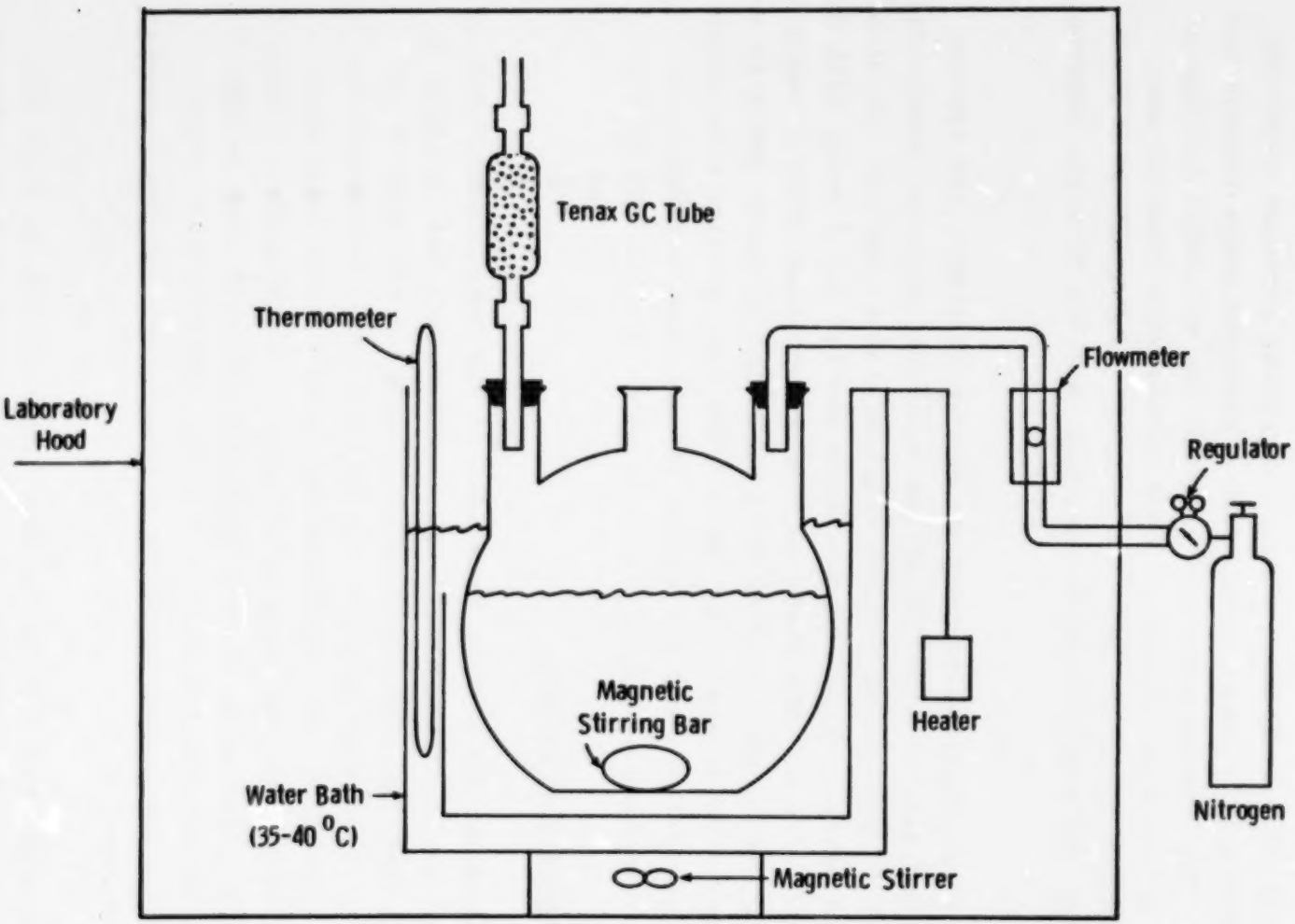


Figure 2. Anaerobic digestion experimental apparatus.

mixing of the reactor contents. The inlet port of the reactor was fitted with a nitrogen supply (including pressure regulator and flowmeter) to insure a continuous nitrogen purge through the system. This was necessary to overcome the potential buildup of methane gas in the reactor. A tube packed with Tenac GC was placed in the exit line from the reactor. The Tenax GC resin would trap any organochromium compounds evolved from the digester flask.

The actual anaerobic digestion run was as follows: the reactor was charged with (1) 1500 ml of the anaerobic digester biological culture, (2) 2500 ml of primary settled sludge, and (3) 500 ml of distilled water. This sludge mixture was run for 4 weeks with no additional inputs. The Tenax GC tube was changed after 2 weeks. After the 4-week run, samples were taken for chromium analysis and for volatile solid analysis. Before the run, samples were taken of both the culture and the sludge for the same analysis. The percent reduction in volatile solids after the run was 56.7%.

4.2.2 Aerobic Digestion

Through contact with plant personnel at the Spauling Road waste treatment plant, Beavercreek, Ohio, information was gathered to indicate that the biological media present in the plant's extended aeration tank would be satisfactory for the laboratory aerobic digestion run. The treatment plant treats basically domestic waste but has several industrial waste sources. Quantities of the biological culture were obtained and used as the inoculum in the aerobic digestion run. The feed was primary sludge from the Dayton treatment plant, as used in the anaerobic digestion run.

The apparatus used for the aerobic digestion run in shown in Figure 3. A 5000-ml flask was utilized as the reactor. Run at room temperature, the flask was put on a magnetic stirrer to

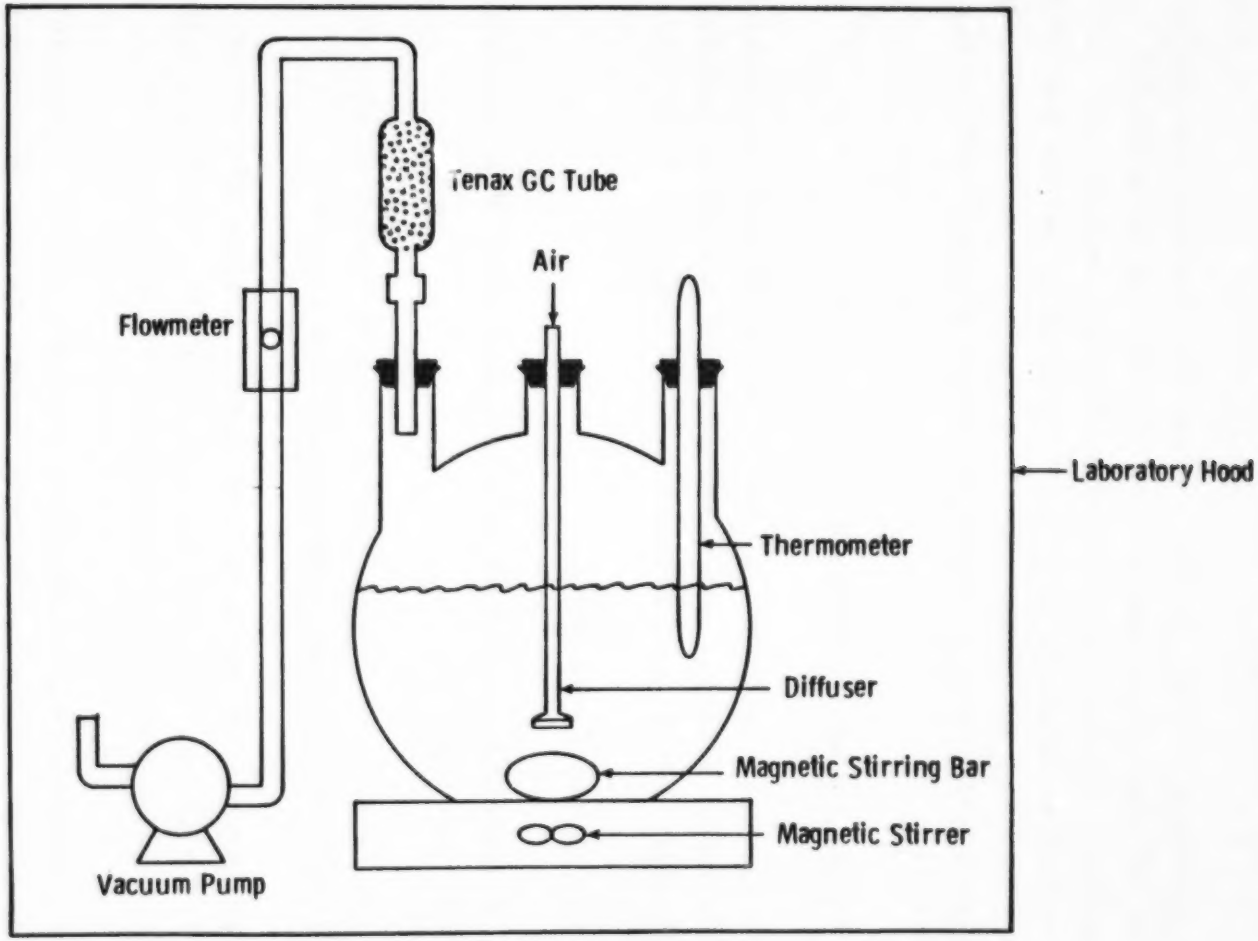


Figure 3. Aerobic digestion experimental apparatus.

insure mixing. A sparger was placed into the reactor, and a vacuum pump, connected to both a flowmeter and Tenax GC tube, was used to pull air into the reactor.

The test procedure was as follows: into the reactor was placed (1) 1000 ml of biological media, and (2) 3000 ml of settled primary sludge. Samples for analysis of both chromium and volatile solids were taken on all fractions both before and after digestion. The digestion was run for 4 weeks as a batch process with no additional inputs. Volatile solids analysis indicated a 42% reduction.

4.3 FRACTIONATION AND EXTRACTION

Newland et al. (11) described a technique for obtaining fractionation of the humic material for examination of the metal content associated with the various fractions. The procedure involved:

1) sample drying at 40°C

2) acid washing with 0.1N hydrochloric acid (HCl) to remove absorbed cations

3) treatment with 0.5N sodium hydroxide (NaOH) to obtain alkali-soluble and alkali-insoluble fractions

4) adjustment of the alkali-soluble fraction to a pH of 1.0 with concentrated HCl to precipiate the humic acid fraction followed by centrifugation and separation

5) adjustment of the remaining solution (total fulvic acid) to pH of 4.8 with 0.1N NaOH to precipitate the β-humus (insoluble fulvic acid fraction)

The four fractions of humus material obtained by this procedure are:

1) humin (nonalkali-soluble material)

2) humic acid

3) β-humus (nonsoluble fulvic acid)

4) soluble fulvic acid

MRC used a modification of this procedure to attempt to obtain information concerning the nature of chromium-humus related complexes. Figure 4 is an overall description of MRC's separation scheme. A 50-ml sample of well mixed sludge was centrifuged. The supernatant liquid was removed and filtered through a 0.4-μm cellulose acetate filter. The liquid portion was retained for analysis to determine the soluble chromium present in the sewage sludge. The solids from this step were then shaken with 20 ml of 0.1N HCl. This sample was then centrifuged and the supernatant liquid analyzed by atomic absorption to determine the cationic chromium content of the sewage sludge. These solids were then shaken with the 20 ml of 0.5N NaOH in a bottle under a nitrogen blanket on a platform shaker for 16 hours. After this period the sample was centrifuged and the liquid removed. Another 20 ml of 0.5N NaOH was then added and the sample shaken for 1 hour, centrifuged, and the liquid removed. Finally, a third 20-ml portion of 0.5N NaOH was added to the solids and the shaking repeated for 1 hour. After centrifuging, the liquid portion of the sample was removed. The three basic liquid extracts were then combined. This solution contained a significant quantity of suspended solids which had not been removed by centrifuging.

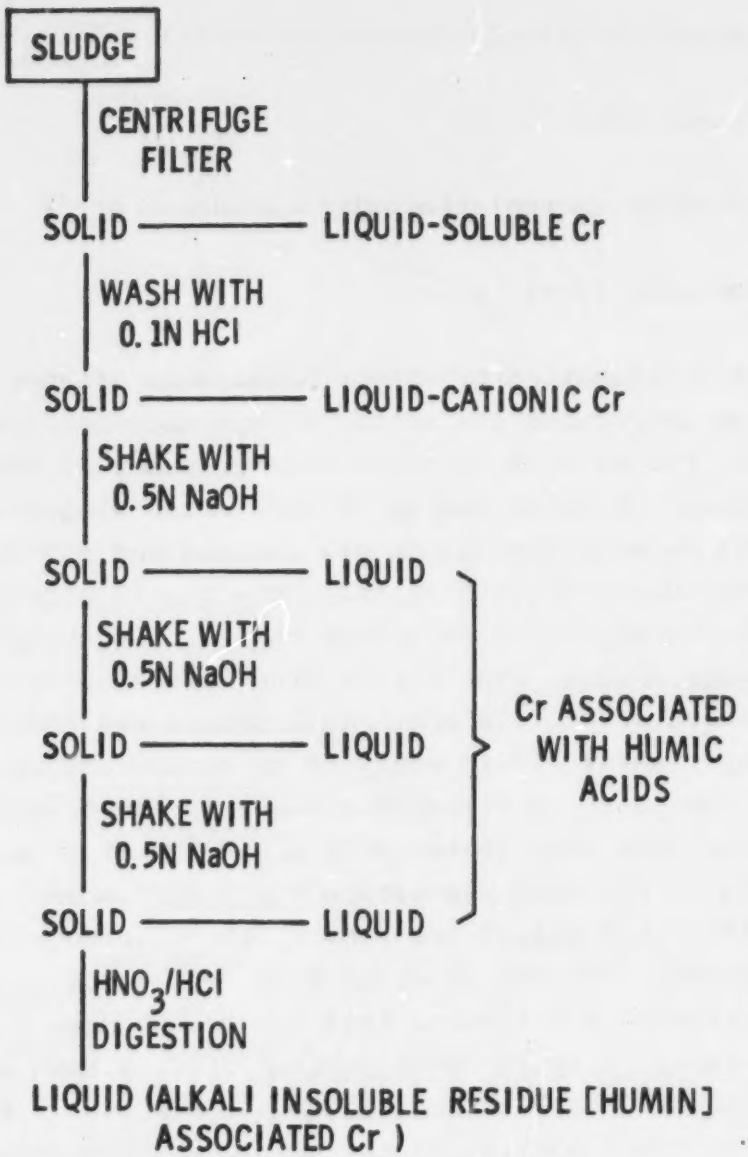


Figure 4. Separation scheme for chromium in sewage sludge.

In order to accurately determine the distribution of chromium between the alkali soluble and insoluble fraction, we found it was necessary to filter the alkali extract. Because of the slimy nature of the solids this was not an easy chore. We found it necessary to filter each sample through 10-, 8-, 5-, 2-, 1.2-, 0.8-, 0.45-, and 0.2-μm filters. The various stages were necessary to permit the filtering at smaller pore sizes; otherwise, the filter pores were very easily plugged. The multitude of filters resulting from each sample was added to the solid from that sample and digested in Teflon beakers with concentrated nitric, sulfuric, and hydrofluoric acids.

4.4 ANALYSIS

All measurements of chromium in the sewage sludge samples were performed by either atomic absorption (AA) spectrophotometry or inductively coupled argon plasma (ICAP) spectroscopy. Each sample was analyzed by digesting the total sample with acid. The total chromium content of these individual fractions was compared with the total chromium in the mixtures in the digestion experiments. The instrument and conditions used for the analysis of chromium in water and the digestion samples are listed in Table 2.

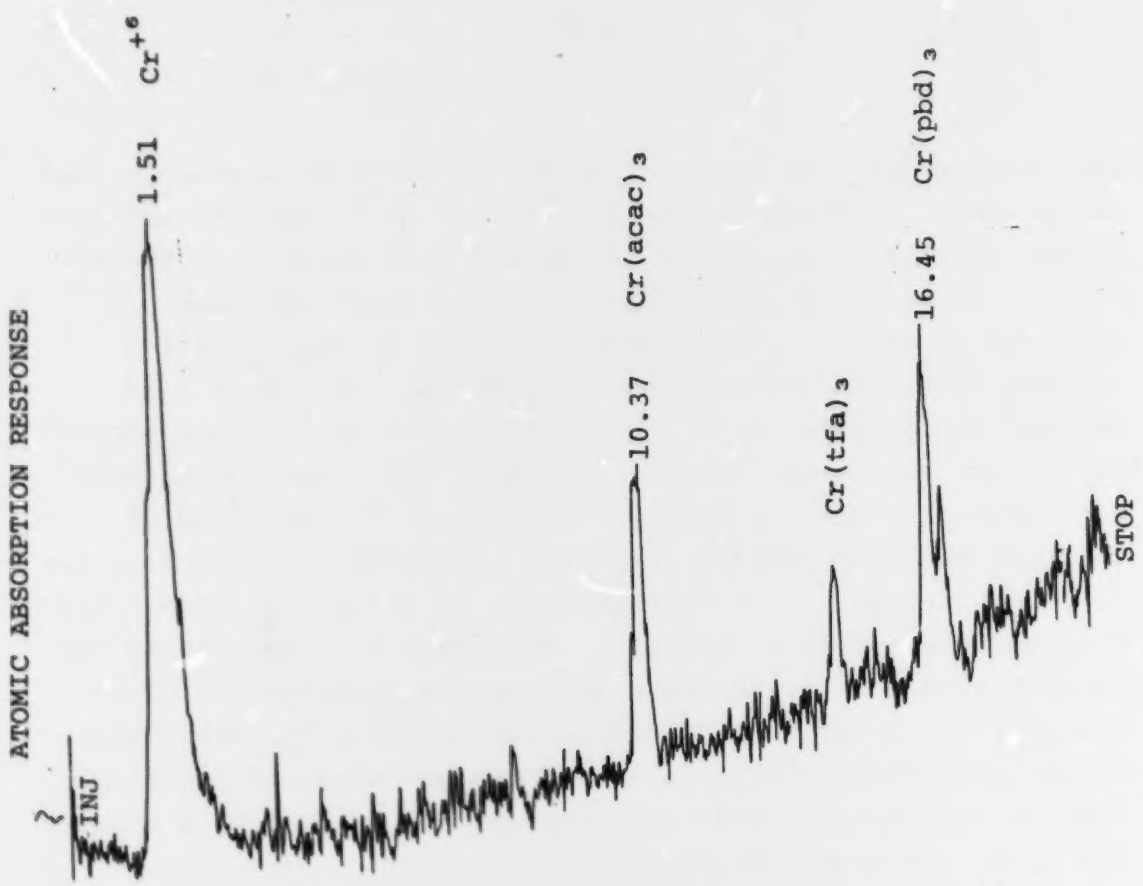
TABLE 2. ATOMIC ABSORPTION CONDITIONS FOR CHROMIUM ANALYSES

Instrument: Perkin-Elmer Model 303
Lamp: Westinghouse chromium hollow cathode
Lamp current: 15 mA
Wavelength: 357.2 nm
Slit: 0.7 nm
Air flow rate: 25 l/min
Acetylene flow rate: 3 l/min
Recorder: Hewlett Packard 3385

In addition to total chromium determinations by atomic adsorption, a high performance liquid chromatograph was interfaced with the atomic absorption spectrophotometer, in a manner similar to one described by Jones (14). The objective of this coupling was to attempt to determine the polarity and molecular weight distribution of chromium-humus acid complexes. The high performance liquid chromatograph was a Micromeritics Model 7115-24, which had been modified with a Model 7100-B pumping system. The interfacing of the HPLC and AA was successfully completed. A mixture of inorganic chromium ion and three organochromium compounds was chromatographed on the HPLC chromatograph. The column used was a Whatman Partisil ODS-1 reverse phase (C-18 terminated). A gradient program from 100% water to 100% methanol over a 20-minute period was employed. The chromatographic trace obtained from the atomic absorption is shown in Figure 5. The conditions for the HPLC are listed in Table 3; atomic absorption conditions were the same as those listed in Table 2.

TABLE 3. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS FOR ORGANOCHROMIUM ANALYSIS

Instrument:	Micromeritics Model 7115-24
Column:	Whatman Partisil ODS-1
Mobile Phase A:	Water
Mobile Phase B:	Methanol
Gradient:	100% A to 100% B in 20 minutes
Gradient shape:	Linear
Flow rate:	20 ml/min
Detector:	Micromeritics Model 785 variable wavelength ultraviolet
Pressure:	∿1500 to 1000 psi



Cr^{+6} = Chromium (VI) ion

$Cr(acac)_3$ = Tris(acetylacetonato) chromium (III)

$Cr(tfa)_3$ = Tris(trifluoroacetonato) chromium (III)

$Cr(pbd)_3$ = Tris(1-phenyl-1,3-butanediono) chromium (III)

Figure 5. Atomic absorption chromatogram of chromium in a mixture of organochromium compounds.

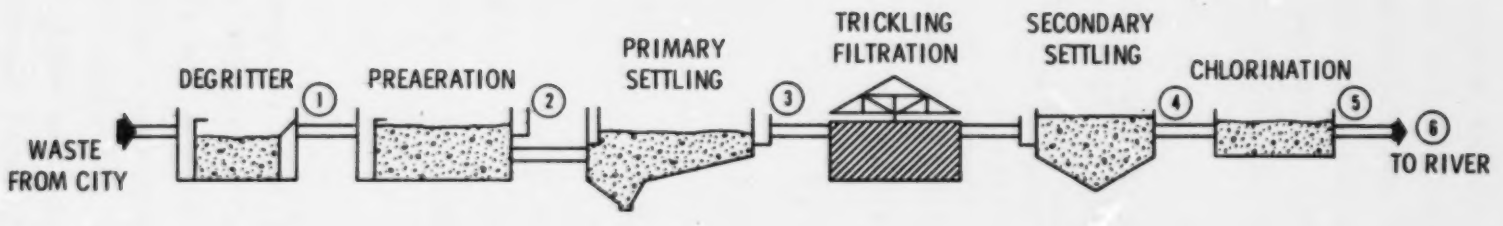
SECTION 5

RESULTS AND DISCUSSION

The results and discussion of this report are divided into four subsections. Section 5.1 describes the results of the analyses of the samples taken at the six points throughout the treatment plant. Section 5.2 gives the results of total chromium analyses of sewage sludge components used in the digestion studies both individually and as mixtures. Section 5.3 is devoted to the results of the fractionation of digester samples before and after the digester studies. This section includes discussions of the analyses of resin tubes for evidence of volatile chromium species which may have been formed during the digester studies. Organic extraction of sludge solids are also discussed in the third section. Section 5.4 is devoted to the results obtained during the study for the distribution of 23 elements among cationic, alkali-soluble, and alkali-insoluble fractions. These results are reported and examined for sludge samples from both aerobic and anaerobic digestions both before and after the digestion studies.

5.1 SEWAGE TREATMENT PLANT SAMPLES

The locations of the sites from which the six sewage treatment samples were taken are shown schematically in Figure 6. The six samples were the influent to the treatment plant taken at the degritter, influent to the primary treatment section of the plant after the preaeration tank, influent to the secondary treatment, influent to the secondary clarifier, effluent from the secondary clarifier, and effluent from the plant after the chlorination. The results of the analyses of these samples for chromium in



1. INFLUENT TO TREATMENT PLANT
2. INFLUENT TO PRIMARY
3. INFLUENT TO SECONDARY
4. INFLUENT TO SECONDARY CLARIFIER
5. EFFLUENT FROM SECONDARY CLARIFIER
6. PLANT EFFLUENT

Figure 6. Schematic of sampling locations at the sewage treatment plant.

both the liquid and solid portions of the sample are shown in Table 4. These results show that while total chromium is reduced during the treatment process, the percentage of chromium in the solids being carried through the plant increases by a factor of more than five times. This indicates the chromium is associated with the smallest of the particles in the sewage sludge.

TABLE 4. DISTRIBUTION OF CHROMIUM THROUGHOUT THE SEWAGE TREATMENT PLANT

Sample	Sample size, ml	Cr concentration of liquid, µg/ml	Solids, mg/ml	Cr concentration of solids, µg/g
1. Influent	25	0.3	3.34	551
2. Influent to primary	25	0.2	3.67	671
3. Influent to secondary	25	<0.2	0.45	2190
4. Influent to secondary clarifier	25	<0.2	0.50	2440
5. Effluent from secondary clarifier	25	<0.2	0.23	2895
6. Plant effluent	25	<0.2	0.27	3769

5.2 TOTAL CHROMIUM ANALYSES

The three sewage sludge components used to prepare mixtures for the digestion studies were analyzed individually for total chromium. The results of these analyses are shown in Table 5. After the digester mixtures were prepared, an aliquot of each was removed and analyzed for total chromium. These same analyses were repeated after the digester studies were completed. The results for theoretical and actual total chromium concentrations

are shown in Table 6. These results show amazingly good agreement for samples as seemingly nonhomogeneous as sewage sludge.

TABLE 5. TOTAL CHROMIUM ANALYSIS RESULTS FOR SEWAGE SLUDGES

Sludge	Cr, µg/g
Primary	127
Secondary	9
Anaerobic	98

TABLE 6. COMPARISON OF TOTAL CHROMIUM VALUES, THEORETICAL AND ACTUAL, OF SLUDGE MIXTURES

Sample sludge	Theoretical Cr, µg/g	Actual Cr before digestion, µg/g	Actual Cr after digestion, µg/g
Aerobic	102	101	99
Anaerobic	97	105	87

5.3 SEWAGE SLUDGE FRACTIONATION

Using the process described earlier in the experimental section, the sewage sludge samples were fractionated. This fractionation process generated a soluble fraction, a cationic (HCl soluble) fraction, a humus-related fraction (alkali soluble), and a humin-related fraction (alkali insoluble). The first two attempts at this processing resulted in very poor mass balances. These problems were attributed to losses during the filtering step. Also, information gained during the analysis of sewage treatment plant samples showed an inaccurate value was obtained for the alkali-soluble fraction if very fine pore size filters were not used. This inaccuracy results from the association of

the chromium with the small diameter particles. If fine-pore filters (0.2 μm) are not used, a larger than actual value is obtained for the content of the alkali-soluble chromium-containing fraction.

The results for the soluble chromium content of sludge sample mixtures from before and after digestion are listed in Table 7. These results are for both anaerobic and aerobic digestions. As can be seen the concentrations are low and do not differ significantly. Results were also obtained with excellent mass balances for the other three fractions of the same four samples. These results are listed in Table 8. The numbers listed for each fraction are for both AA spectrophotometry and ICAP spectroscopy. The two techniques show fairly good agreement for the chromium content. The chromium concentrations are listed as micrograms per gram of dried sludge. The estimated error for the two techniques was ±10-15%. The alkali-soluble (humus-related fraction) chromium was found to increase from 7.9% to 8.2% of the total chromium during the month-long aerobic digestion. For this same fraction the chromium content decreased from 9.0% to 2.4% of the total chromium during the month-long anaerobic digestion. This means that there is little to no significant change in the way in which chromium is bound in the aerobic process. Second, the chromium becomes more bound to the larger, less soluble humin fraction during anaerobic digestion.

TABLE 7. CHROMIUM CONCENTRATION IN THE LIQUID PORTION OF SEWAGE SLUDGE MIXTURES

Digester mixture	Cr, μg/ml
Aerobic before	0.17
Aerobic after	0.15
Anaerobic before	0.20
Anaerobic after	0.16

TABLE 8. COMPARISON OF ATOMIC ABSORPTION AND INDUCTIVELY COUPLED ARGON PLASMA ANALYSIS OF CHROMIUM IN SEWAGE SLUDGE FRACTIONS

	Chromium, µg/g							
	HCl		NaOH		Solid		Total	
Digester mixture	AA	ICAP	AA	ICAP	AA	ICAP	AA	ICAP
Aerobic before	-	2.0	172.5	144	1500	1665	1672.5	1811.0
Aerobic after	-	1.3	136.8	149	1620	1652	1756.8	1802.3
Anaerobic before	-	1.6	164.9	166	1462	1670	1626.9	1837.6
Anaerobic after	-	0.5	46.2	45.2	1645	1825	1691.2	1870.7

Initial plans for the program included neutralization of the alkali fractions followed by HPLC-AA analysis of these neutralized fractions. Unfortunately when the alkali-soluble fractions were neutralized, a significant portion of the sample precipitated. After filtering the precipitate, the filtrate was found to be too low in chromium concentration for HPLC-AA. When this filtrate was concentrated, more precipitate was formed and it was found to be impossible to increase the chromium content of the liquid portion to a level sufficient for detection by HPLC-AA.

Similar results were obtained for alkali-soluble fractions which were adjusted to pH 8. These samples were going to be used with Sephadex gels for molecular weight determination of the organochromium fraction. However, when concentration was attempted, the chromium content of the aqueous portion was never high enough for gel-AA analysis.

Soxhlet extraction of dried sludge samples from the four samples were conducted with methanol for 24 hours. These extracts were then analyzed and found to contain no detectable chromium.

The Tenax GC tubes which were used to collect any volatile chromium compounds during the digestion experiments were desorbed with methanol. A total of four tubes, two from aerobic and two from anaerobic digestion, were desorbed. Each tube had been

used for collection for a 2-week period. The tubes were desorbed with 4 ml of methanol. This volume had been found to be sufficient for recovery of greater than 90% of most compounds. Analysis of the methanol desorption solution by atomic absorption showed no detectable chromium from any of the four tubes. These methanol solutions were also examined by HPLC-AA and found to contain ultraviolet-absorbing compounds but no detectable organochromium compounds.

5.4 RESULTS FOR OTHER ELEMENTS

Since ICAP spectroscopy was chosen to check the atomic absorption results for the chromium content of each fraction, a survey of the concentrations of 22 other elements was conducted. Table 9 lists the elements and their abbreviations. The results for the HCl (cationic), NaOH (alkali-soluble) and solids (alkali-insoluble) fractions are listed in Tables 10a and 10b. The mass balances for the elements, except for Ag, Al, B, Si and Ti, are fairly consistent. These results show homogeneity was obtained for the sludge samples, and the digestion processes used were very effective for reducing the alkali-soluble metal content of sewage sludge.

In order to carry this investigation of the elements one step farther, a determination was made of the alkali-soluble fraction content for each element as a percentage of the total concentration of that element. The results for these determinations are listed in Table 11. Along with the percent extract in both before and after digestion sludge samples, the percent change is listed. The following elements were found to be reduced most by aerobic digestion: Ag, Al, Cu, Mo, Ni and V. For another group of elements the anaerobic digestion process results in the greatest percent decrease in extractability: B, Ba, Cd, Co, Cr, Fe, Mg, Mn, Pb, Sr and Ti. Finally, some elements did not undergo a significantly different change in either process: P, Sb, Si, Sn and Zn.

TABLE 9. ELMENTS ANALYZED IN SEWAGE SLUDGE

Element	Abbreviation
Silver	Ag
Aluminum	Al
Boron	B
Barium	Ba
Beryllium	Be
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Magnesium	Mg
Manganese	Mn
Molybdenum	Mo
Nickel	Ni
Lead	Pb
Phosphorus	P
Antimony	Sb
Silicon	Si
Strontium	Sr
Titanium	Ti
Yttrium	Y
Zinc	Zn

TABLE 10a. CONCENTRATION OF SELECTED ELEMENTS IN FRACTIONS OF SEWAGE SLUDGE SAMPLES

	Concentration, µg/g										
Aerobic before	Ag	Al	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Mg
HCl	8.8	13.8	13.6	1.4	-	-	2.0	2.0	0.7	4.3	1488
NaOH	45.0	1609	106.8	27.5	-	64.5	14.7	144	391	803	93
Solids	138	4022	426	184	1.4	128	51.5	1665	873	10554	3751
Total	191.8	5645	546.4	212.9	1.4	192.5	68.2	1811	1264.7	11361	5332
Aerobic after											
HCl	7.8	7.6	6.2	0.8	-	0.03	1.1	1.3	0.9	0.2	683
NaOH	28.4	1263	34.0	25	-	38	4.7	149	227	813	139
Solids	335.3	7048	155	312	2.3	156	53	1652	1147	9918	4532
Total	371.5	8318.6	195.2	338.4	2.3	194.03	58.8	1802.3	1374.9	10731	5354
Anaerobic before											
HCl	6.1	9.1	3.8	1.6	-	<0.03	1.5	1.6	1.4	3.3	831
NaOH	45.9	1411	99.1	30.4	-	68	6.4	166	427	1067	166
Solids	194	4484	88	291	1.7	130	52	1670	1088	11856	4375
Total	246	5904.1	190.9	323	1.7	198.03	59.9	1837.6	1516.4	12926.3	4372
Anaerobic after											
HCl	2.0	-	5.0	0.7	-	-	1.4	0.5	-	1.0	786
NaOH	43.3	1157	54	5.4	-	33.4	1.4	45	262	246	89
Solids	291	5417	83	330	2.4	176.3	60	1825	1205	11488	5018
Total	336.3	6574	142	336.1	2.4	209.7	62.8	1870.5	1467	11735	5893

TABLE 10b. CONCENTRATION OF SELECTED ELEMENTS IN FRACTIONS OF SEWAGE SLUDGE SAMPLES

	Concentration, µg/g											
	Mn	Mo	Ni	Pb	P	Sb	Si	Sn	Sr	Ti	Y	Zn
Aerobic before												
HCl	-	-	10	3.6	144	3.3	348	-	16.7	0.3	9.4	1.1
NaOH	9.3	18.7	168	105	5392	40.3	1341	254	17.1	46.2	31.7	2383
Solids	134	49.7	416	780	10403	175	7237	478	505	1411	116	3805
Total	143.3	68.4	594	888.6	15939	218.6	8926	732	538.8	1457.5	157.1	6189.1
Aerobic after												
HCl	1.4	0.5	15.0	5.5	46	1.3	98	-	26.2	0.3	6.3	0.5
NaOH	9.4	7.4	133	135	4041	20.8	1499	151	16.7	46	25.6	1068
Solids	155	56.7	500	688	12576	192	9211	454	565	4055	174	5180
Total	165.8	64.6	648	828.5	16663	214.1	10808	605	607.9	4101.3	205.9	6248.5
Anaerobic before												
HCl	5.5	0.4	20.7	2.1	132	0.05	87	0.2	57	0.9	7.8	1.6
NaOH	11	15.5	136	141	4234	26.9	1379	256	21	65	24.6	1992
Solids	155	51.3	512	761	11482	158	6741	373	570	2127	125	4194
Total	171.5	67.2	668.7	904.1	15848	184.95	8207	629.2	648	2193	157.4	6187.6
Anaerobic after												
HCl	1.6	-	5.3	-	138	-	67	0.9	35.4	0.02	6.4	-
NaOH	2.1	10.2	125	88	3258	17.5	1098	202	5.4	20.3	22.1	966
Solids	171	67	529	954	12493	205	5202	446	583.8	3255	147	5450
Total	174.7	77.2	659.3	1042	15889	223.2	6367	648.9	624.6	3275.32	175.5	6416

TABLE 11. DIGESTION EFFECTS ON THE PERCENTAGE OF SELECTED ELEMENTS IN THE 0.5N NaOH EXTRACTABLE FRACTION OF SEWAGE SLUDGE

	Percent*			
Element	Before aerobic digestion	After aerobic digestion	Before anaerobic digestion	After anaerobic digestion
Ag	23.5	7.6	18.7	12.7
Al	28.5	15.2	23.9	17.6
B	19.5	17.9	52	38.0
Ba	12.9	7.5	9.4	1.6
Be	-	-	-	-
Cd	33.5	19.5	34.3	15.9
Co	21.5	8.0	10.7	2.2
Cr	7.9	8.2	9.0	2.4
Cu	30.8	16.5	28.2	17.8
Fe	7.0	7.6	8.2	2.1
Mg	1.7	2.6	3.1	1.5
Mn	6.5	5.6	6.4	1.2
Mo	27.3	11.5	23.1	15.2
Ni	28.3	20.5	20.4	18.9
Pb	11.8	16.3	15.6	8.4
P	33.8	24.3	26.7	20.5
Sb	18.4	9.7	14.5	7.8
Si	15.0	13.9	16.8	17.2
Sn	34.7	25.0	40.7	31.1
Sr	3.2	2.7	3.2	0.9
Ti	3.2	1.1	3.0	0.6
V	20.1	12.4	15.6	12.6
Zn	38.5	17.0	32.2	15.1

*Percentages are based on the total concentration of each element in the undigested, unextracted sludge.

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